Morphology Behavior of Polysulfone Membranes Made from Sustainable Solvents

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Abstract: In a previous study, we demonstrated a change in membrane morphology and gas separation performance by varying the recipe of a casting solution based on polysulfone in a certain solvent system. Although all results were reproducible, all used solvents were harmful and not sustainable. In this study, the solvents tetrahydrofuran (THF) and N,N-dimethylacetamide (DMAc) are replaced by the more sustainable solvents 2-methyl-tetrahydrofuran (2M-THF), N-butyl pyrrolidinone (NBP) and cyclopentyl methyl ether (CPME). The gas permeation performance and, for the first time, morphology of the membranes before and after solvent replacement were determined and compared by single gas permeation measurements and SEM microscopy. It is shown that THF can be replaced by 2M-THF and NBP without decreasing the gas permeation performance. With CPME replacing THF, no membranes were formed. Systems with 2M-THF as a THF alternative showed the best gas permeation results. Permeances for the tested gases oxygen (O₂), nitrogen (N₂), carbon dioxide (CO₂) and methane (CH₄) were 5.91 × 10⁻², 8.84 × 10⁻³, 4.00 × 10⁻¹ and 1.00 × 10⁻² GPU, respectively. Permselectivities of those membranes for the gas pairs O₂/N₂, CO₂/N₂ and CO₂/CH₄ were 6.7, 38.3 and 34.0, respectively. When also replacing DMAc in the solvent system, no or only porous membranes were obtained, even if the precipitation procedure was adjusted. These findings indicate that a complete replacement of the solvent system without affecting the membrane morphology or gas permeation performance is not possible. By varying the temperature of the precipitation bath, the formation of mechanically stable PSU membranes is possible only if THF is replaced by 2M-THF.

Keywords: polysulfone; membranes; sustainable solvents; gas separation; biogas; morphology; gas separation membranes

1. Introduction

In the wake of environmental and climate problems, a new field of application is opening for chemistry and especially for polymer materials in the 21st century. The use of most contemporary solvents is not sustainable. In the interests of developing more environmentally friendly and more sustainable processes and products, alternatives to conventional solvents have become increasingly relevant. This topic also affects the research area of polymeric membranes, in particular those based on polymer solutions. In non-solvent-induced phase separation (NIPS), the most versatile method, tetrahydrofuran (THF), N,N-dimethyl acetamide (DMAc) as well as N,N-dimethyl formamide (DMF) and N-methyl-2-pyrrolidinone (NMP) are traditionally used [1–6]. Besides issues regarding disposal, these solvents pose a health hazard. Additionally, the risk of long-term problems regarding human health and environmental pollution is growing [7,8]. The European Chemical Agency (ECHA) will also restrict the industrial use of NMP, DMAc and DMF [9].

Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) was implemented by the European Union in 2007. The aim of REACH is to improve the protection of human health and the environment. This includes the promotion of alternative
methods. In the case of membrane fabrication, this means, for example, the replacement of harmful solvents. With respect to this work, this requires the replacement of THF and DMAc. These solvents are suspected of causing cancer or may damage the unborn child. It is likely that THF and DMAc will undergo restriction like NMP did in 2020.

In the literature, several different fabrication processes are described for flat sheet membranes. Most prevalent are non-solvent-induced phase separation (NIPS), temperature-induced phase separation (TIPS) and evaporation-induced phase separation (EIPS). The NIPS process has been researched intensively over the decades and is used to fabricate flat sheet PSU membranes in this study [1,6,10–16]. In this process, a polymer is dissolved in an organic solvent or solvent system. After dissolution of the polymer, it is cast to a film (protomembrane) and put into a precipitation bath. By immersion into a precipitation bath, the miscibility gap of the protomembrane (solvent–polymer system) is reached, resulting in phase separation. Liquid–liquid demixing occurs and a polymer-depleted and a polymer-rich phase is formed within the protomembrane. The polymer-depleted phase causes large finger-like, drop-shaped or smaller bubble-shaped voids [17,18]. The small and polar water molecules diffuse one to two orders of magnitude faster from the precipitation bath into the protomembrane compared to organic solvents diffusing from the protomembrane into the precipitation bath, which often results in large voids [19]. The polymer-rich phase forms the resulting membrane.

Based on a polymer dissolved in a water-soluble organic solvent and water as a precipitation medium, the structure of a membrane can be estimated by the solubility parameters of the polymer, organic solvent and water [20]. These estimations are built on assumptions and practical experience based on empirical and physicochemical data [21]. Water is often used as a precipitation medium because most membrane polymers are not soluble in water but are in organic solvents. This causes the precipitation of a polymer dissolved in an organic solvent when put into water. For this purpose, the organic solvents need to be completely miscible with water [19]. When membranes are produced by NIPS, different membrane morphology, porosity and separation properties can be observed depending on various parameters such as precipitation medium, polymer concentration in solution, solvent system, temperature of the precipitation bath, atmosphere, residence times, thickness of the wet film, support, post treatment, etc. [3,6,15,16,18,19,22–28]. Careful control of these parameters allows control of the resulting membrane morphology.

If all parameters are chosen to create a dense gas separation layer in a membrane, the latter can be used for gas separation. Gas separation is based on the different permeation behaviors of different gases in a membrane. The permeation of gases in a membrane can be described in two steps. Firstly, the sorption of gases into the membrane is required [29]. After this step has taken place, the second step, namely diffusion, can follow. Directional transport through a membrane only occurs in the presence of an external driving force [30–33]. This driving force is a difference in the chemical potential between the feed and the permeate site of a membrane, applied via a pressure difference in the case of gas separation.

In membrane fabrication, over 90% of industrial waste results from wastewater contamination by solvents used in membrane fabrication, amounting to about 20–100 billion liters annually [34–36]. The recycling of wastewater is desirable but not always applicable because of requirements regarding purity and regulations [37,38]. Based on the 3Rs for the circular economy, reduce, reuse and recycle, reuse is not an option, since waste from membrane fabrication must be treated. Therefore, reduce and recycle are applicable, where reduce should be the most favorable option [39,40]. To overcome challenges presented by the use of harmful solvents, the use of more sustainable solvents is an appropriate alternative.

Research on more sustainable membrane materials and solvents is a growing field [38,41–45]. Recent research in the field of sustainable solvents deals with Rhodiavol PolarClean [7,46,47], Cyrene [7], dimethyl sulfoxide (DMSO) [48–50], γ-valerolactone (GVL) [51], dimethyl isosorbide (DMI) [34] and NBP [52,53]. Moreover, toxicity and hazardousness are just two
aspects to be taken into consideration for more sustainable solvents. More aspects, such as the energy required to produce alternative solvents and the potential of recycling or disposal, must also be considered [54].

The aim of this study is to control the morphology of membranes produced via the NIPS process when more sustainable solvents are used. Since all solvents have different solubility parameters and therefore affect membrane morphology, this study shows for the first time that even with more sustainable solvents and by varying precipitation bath temperatures it is possible to control the membrane morphology of polysulfone gas separation membranes.

2. Materials and Methods

In this section, the materials and methods used for this study are listed and explained to give readers or interested people the opportunity to reproduce our experiments.

2.1. Materials

Polysulfone, P-3500 LCD MB7 (78.6 kg/mol, Solvay, Brussels, Belgium), was used to fabricate PSU flat sheet membranes. Polydimethylsiloxane (Elastosil RT 625 A and B, PDMS, Wacker Chemie AG, Munich, Germany) was used to coat the fabricated polysulfone membranes. Tetrahydrofuran (99.9%; Carl Roth GmbH + Co. KG, Karlsruhe, Germany), N,N-dimethyl acetamide (99.5%; Carl Roth GmbH + Co. KG, Karlsruhe, Germany), methanol (99.9%; Carl Roth GmbH + Co. KG, Karlsruhe, Germany), cyclopentyl methyl ether (99%; Carl Roth GmbH + Co. KG, Karlsruhe, Germany), N-butyl-2-pyrrolidinone (99.5%; Carl Roth GmbH + Co. KG, Karlsruhe, Germany), 2-methyl-tetrahydrofuran (GPR RECTAPUR, VWR, Radnor, PA, USA) and n-heptane (≥95%; Carl Roth GmbH + Co. KG, Karlsruhe, Germany) were used as-received. According to Henis and Tripodi, even defects in the range of 5 to 10 Å in the gas separation layer lead to a significant reduction in permselectivity [55,56]. Therefore, membranes were coated with PDMS to close those defects which may occur. If larger defects occur in the gas separation layer, significantly worse permselectivity of the PDMS coating compared to PSU are likely to be observed [56,57].

2.2. Membrane Preparation

The desired amount of solvent was added to a capped flask and PSU pellets were added. Polysulfone and solvents were mixed in the closed flask for 16 h on a roller bench until a homogenous, yellowish polymer solution was obtained. To shift the solubility equilibrium closer to the demixing point, a certain mass of methanol was added to the polymer solution drop by drop and further mixed until the solution was homogenous again. The obtained casting solution was then poured onto a glass plate and fabricated to a polymer film with the aid of a casting knife set to a 250 µm gap height at a speed of 17 mm/s (1 m/s). The glass plate was immersed in the precipitation bath for thirty minutes immediately after casting. To wash away remaining solvents, the precipitated membranes were rinsed with distilled water for about one minute on each side. Afterwards, the washed membranes were left to dry at room temperature in a dust-free box for at least 16 h. Before testing, PSU membranes were coated with PDMS (9:1 = component A:component B, 70% by mass in n-heptane) after they had dried.

2.3. Determination of Membrane Thickness

The magnetic inductive method is a type of non-destructive material testing for analyze the thickness d of electrically insulating materials or coatings on ferromagnetic substrates. For this purpose, the non-magnetic material—in this case a polymer membrane—is placed on a steel plate and measured at several points. The probe consists of an iron core wrapped with a measuring coil and an excitation coil to which a low-frequency alternating current is applied, which creates an alternating magnetic field around the iron core.

If the probe approaches the material and thus also the ferromagnetic base during the measurement, the magnetic field increases. Depending on the distance or the layer
thickness of the non-magnetic material, a voltage is detected by the measuring coil. This voltage is proportional to the thickness of the non-magnetic material. The gained voltage is evaluated digitally. The morphology of membranes is not considered in these kinds of measurements. The measuring principle is shown in Figure 1.

![Measuring principle of magnetic inductive layer thickness measurement.](image)

Figure 1. Measuring principle of magnetic inductive layer thickness measurement.

In this work, a device from Helmut FISCHER (Sindelfingen, Germany) from the FMP 10–20 series with a stainless-steel plate as a ferromagnetic base was used. This device measures the composite of PSU and PDMS, as well as both components individually.

2.4. Scanning Electron Microscopy

To examine the membrane structures obtained, scanning electron micrographs were taken with an EVO 15 SmartSEM (Carl Zeiss NTS, Oberkochen, Germany). For this purpose, the samples were immersed in liquid nitrogen, broken and were then fixed to a conductive carrier before they were vapor-deposited with a 4 nm-thick layer of gold. The samples were measured at an acceleration voltage of 9.46–20.00 kV. The SEM images in this paper only include membrane samples from polysulfone membranes without a PDMS protective layer, since the focus of this work is on PSU flat sheet membranes.

2.5. Gas Permeation Measurements

Single-gas permeation tests were conducted using a time-lag apparatus and the differential-pressure method. Permeances of the coated membranes for oxygen (O₂), nitrogen (N₂), methane (CH₄) and carbon dioxide (CO₂) were determined using the time-lag method at 25 °C. The measurements were performed after an evacuation period of 1.5 h after every sample exchange and of twelve time-lags (Θ) in between the measurements (minimum 3 min, maximum 6 h). To minimize measurement uncertainties, each single-gas was measured twice and at different feed pressures of 390 mmHg (520 mbar) and 600 mmHg (800 mbar). The permeate pressure was set to 7.5 × 10⁻⁵ mmHg (1 × 10⁻⁴ mbar) at the beginning of each measurement [58].

Permeances can be calculated by Equation (1):

\[
P_i = \frac{V(\text{STP})}{A \cdot \Delta p \cdot t}
\]

where \(V(\text{STP})\) is the volume of gas that has passed through the membrane at standard temperature and pressure, \(A\) is the effective membrane area, \(\Delta p\) is the pressure difference between the feed and permeate side of the membrane and \(t\) is the time that has passed in seconds. Permeance is expressed in gas permeation units (GPU), which is defined by:

\[
1 \text{ GPU} = 1 \times 10^{-6} \frac{\text{cm}^3(\text{STP})}{\text{cm}^2\cdot\text{cmHg} \cdot \text{s}}
\]
The uncertainty of measurement for the setup in this study lies at \(2.22 \times 10^{-3}\) GPU.

The apparatus measures the time-dependent pressure increase of the permeate to obtain a time–pressure curve for every gas. A schematic representation of such a curve is given in Figure 2.

Figure 2. Exemplary depiction of a time–pressure curve obtained from the time-lag measurement. The time-lag is setting the time for evacuation between every single-gas measurement.

The permselectivity \(a_{A,B}\) of a membrane in relation to two gases A and B is also called ideal selectivity and is determined according to Equation (3) from the ratio of the permeances of gases A and B.

\[
a_{A,B} = \frac{P_A}{P_B}
\]

(3)

2.6. Solubility

The solubility of polymers in certain solvents can be estimated via Hansen Solubility Parameters (HSPs). These parameters describe the total energy of vaporization of components considering molecular interactions based on dispersive forces \(\delta_d\), polar forces \(\delta_p\) and hydrogen bonding \(\delta_h\). By visualization in a 3-dimensional Hansen sphere model, solubility parameter distances can be obtained. The “distances” \(R_d\) between the Polymer (P) and Solvent (S) can also be calculated as shown by Hansen and Skaarup [59]:

\[
R_d = \sqrt{4(\delta_{d,S} - \delta_{d,P})^2 + (\delta_{p,S} - \delta_{p,P})^2 + (\delta_{h,S} - \delta_{h,P})^2}
\]

(4)

With the relative energy distance, RED, which is equal to \(R_a/R_0\) where \(R_0\) is the radius of the sphere of the Hansen sphere model, one has a qualitative criterion to estimate if a solvent is able to dissolve a certain polymer. The \(R_0\)-value for PSU is, in this study, set to a value of 8. If the RED exceeds a value of 1, the polymer is probably not soluble. At RED-values below 1, a solvent is probably able to dissolve a certain polymer. If the RED-value is 1, the polymer is partially soluble [20,34].

To calculate the RED in this study, the HSPiP 6th Edition (6.0.04) software was used.

3. Results and Discussion

In a previous study, we reported the fabrication of PSU membranes using traditional solvents [18]. Electron microscopy revealed a gas separation layer of around 20 to 50 nm and a sponge-like support structure. The thickness of the overall membrane was 100 µm. This membrane structure is favorable in gas separation applications at elevated pressures [60]. The composition of the casting solution and casting conditions of these membranes are given in Table 1.
Table 1. Compositions of membranes with harmful solvents [18].

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value and Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition of the casting solution</td>
<td>25 wt% PSU, 58.28 wt% THF, 3.72 wt% DMAc, 13 wt% MeOH</td>
</tr>
<tr>
<td>Gap height of casting knife</td>
<td>250 µm</td>
</tr>
<tr>
<td>Casting speed</td>
<td>17 mm/s</td>
</tr>
<tr>
<td>Free-standing duration</td>
<td>≈3 s</td>
</tr>
<tr>
<td>Precipitation medium</td>
<td>Water for 4 min</td>
</tr>
<tr>
<td>Washing step</td>
<td>60 s under running water (top and bottom side each)</td>
</tr>
<tr>
<td>Drying step</td>
<td>16 h in fume hood</td>
</tr>
<tr>
<td>Lab temperature</td>
<td>21 °C</td>
</tr>
<tr>
<td>Post treatment</td>
<td>Coating with PDMS-layer after drying @ RT</td>
</tr>
</tbody>
</table>

Data reproduced from [18] showed the morphology depicted in Figure 3. This morphology includes a very thin separation layer and a sponge-like support structure beneath the separation layer.

Figure 3. (Left): cross section of a non-layered PSU flat sheet membrane fabricated according to conditions shown in Table 1. (Right): enlarged view with a dense separation layer between the dashed lines and sponge-like support structure below.

Solvents used to produce the membranes shown above are listed as toxic and harmful to the environment [5,7,8]. The transition to greener alternatives, however, is not trivial. In an attempt to quantify the process of dissolution, so-called solubility parameters are used [7]. These parameters affect the resulting membrane structure during precipitation, leading to different mechanical stabilities and separation performances [18,23]. Among other parameters, the size of the solvent molecules is reported to influence the gas separation performance of the membranes [61].

3.1. Solvent Exchange

The solvent system of membranes listed in Table 1 consists of two solvents and one co-solvent. Since the latter has a completely different effect on the solution and therefore the resulting membrane, only the two solvents, namely THF and DMAc, are exchanged in this study. Methanol therefore remains part of all test systems. The exchange of methanol is the subject of ongoing research.

As an alternative for THF and DMAc, three more sustainable solvents were provided:

- N-Butyl-2pyrrolidinone (NBP);
- 2-Methyl-Tetrahydrofurane (2M-THF);
- Cyclopentyl methyl ether (CPME).

These solvents were used as both THF and DMAc replacements. These solvents are considered as more sustainable because some principles of the twelve principles of...
Green Chemistry are applicable for the chosen solvents. They all are less toxic and less harmful for human health and the environment compared to THF and DMAc, which refers to principles 3, 4 and 12. Additionally, 2M-THF is a biosourced solvent, which refers to principle 7. [45,62] The chemical structures of all solvents are given in Table 2.

**Table 2.** Chemical structures of all solvents used in this study.

<table>
<thead>
<tr>
<th>Chemical Structure</th>
<th>Solvent Name</th>
<th>Boiling Point</th>
<th>RED (PSU)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="THF structure" /></td>
<td>THF</td>
<td>66 °C</td>
<td>0.80</td>
</tr>
<tr>
<td><img src="image" alt="DMAc structure" /></td>
<td>DMAc</td>
<td>166 °C</td>
<td>0.84</td>
</tr>
<tr>
<td><img src="image" alt="NBP structure" /></td>
<td>NBP</td>
<td>240 °C</td>
<td>0.66</td>
</tr>
<tr>
<td><img src="image" alt="2M-THF structure" /></td>
<td>2M-THF</td>
<td>78 °C</td>
<td>0.95</td>
</tr>
<tr>
<td><img src="image" alt="CPME structure" /></td>
<td>CPME</td>
<td>106 °C</td>
<td>1.03</td>
</tr>
</tbody>
</table>

3.1.1. Replacement of THF and DMAc

The aim of this work is to observe the influence of the solvent system on membrane formation and the resulting morphology. In order to allow comparison of the traditional solvent system with more sustainable alternatives, the individual amounts of solvent were not changed within the solvent system.

In a first step, THF was replaced by NBP, 2M-THF and CPME for membrane preparation. Solvent systems that result in the formation of functional membranes after the replacement of THF were tested for the replacement of DMAc in the next step of solvent exchange.

Table 3 shows all tested solvent systems in which THF, and DMAc were replaced.

**Table 3.** Solvent systems with working THF alternatives in which DMAc was replaced additionally.

<table>
<thead>
<tr>
<th>Solvent System</th>
<th>Solvent 1</th>
<th>Solvent 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>NBP</td>
<td>DMAc</td>
</tr>
<tr>
<td>M2</td>
<td>2M-THF</td>
<td>DMAc</td>
</tr>
<tr>
<td>M3</td>
<td>CPME</td>
<td>DMAc</td>
</tr>
<tr>
<td>M4</td>
<td>NBP</td>
<td>2M-THF</td>
</tr>
<tr>
<td>M5</td>
<td>NBP</td>
<td>CPME</td>
</tr>
<tr>
<td>M6</td>
<td>2M-THF</td>
<td>NBP</td>
</tr>
<tr>
<td>M7</td>
<td>2M-THF</td>
<td>CPME</td>
</tr>
</tbody>
</table>

After all solvent tests were completed, a solvent system was selected to vary its parameters in membrane formation, i.e., temperature of the precipitation bath. This decision was based on the properties of the membranes of these solvent systems. The evaluation criteria were as follows:
• gas permeance;
• stability;
• morphology;
• sustainability.

The first is the most important and decisive factor, as it affects the separation performance of the membranes. Morphology can possibly be controlled by changing the composition of the solution or process parameters in membrane formation. In the case of several equal solvent systems, the solvents used per system were compared in terms of sustainability and the more sustainable system selected.

3.1.2. Variation of Temperature of the Precipitation Bath

In this series of experiments, the temperature of the precipitation bath, which is used in the standard process at room temperature, was changed. Membranes were prepared at precipitation bath temperatures of 0 °C and 60 °C. These values were chosen to cover the temperature range between the freezing point of the precipitation medium and the evaporation temperature of the co-solvent methanol.

Diffusion in liquids is described by the Stokes–Einstein Equation:

\[ D = \frac{k_B T}{6\pi\eta r} \]  

Equation (5) shows that the diffusion coefficient \( D \) depends on the temperature \( T \) of the environment, the viscosity \( \eta \) and, assuming that the molecules are spherical, on the radius \( r \) of these molecules. The Boltzmann constant \( k_B \) (1.38 × 10\(^{-23}\) J K\(^{-1}\)) is the conversion factor for absolute temperature in relation to absolute, physical zero in energy. It should also be noted that this connection is independent of the charge of the diffusing particles and a proportionality of the friction force to the molecular speed is assumed.

According to Equation (5), it can be assumed that the temperature of the precipitation bath influences the diffusion of the solvent and the precipitation medium and thus also the morphology of the resulting membranes. As the temperature increases, the rate of diffusion increases.

By reducing the precipitation bath temperature, a more homogeneous sponge-like membrane morphology can be expected, while a less favorable morphology is expected at an elevated temperature.

3.2. Replacement of THF

Membranes prepared with NBP as the solvent showed insufficient stability after four minutes of precipitation. Within this time, solvent exchange was not completed, which leads to the redissolution of the membranes whilst drying. During precipitation, the membranes changed from transparent to white. In the redissolution step, membranes changed back from white to transparent and they were getting softer compared to directly after precipitation. This is because water from the precipitation bath evaporates faster than NBP in the drying step and therefore a redissolution takes place. Water has a boiling point of 100 °C and NBP has a boiling point of 240.6 °C, resulting in faster evaporation of water compared to NBP causing redissolution.

To overcome this issue, the precipitation time was adjusted to 20 min. After this period, the solvent was replaced by water in a manner that no redissolution occurred and all membranes could be left to dry. No redissolution was observed when 2M-THF was used as a THF alternative, regardless of the precipitation time. For the sake of comparability, precipitation time was increased to 20 min for all following experiments.

As seen in Figure 4, the membrane structure of membranes prepared from NBP and 2M-THF is different to membranes prepared from THF.
leads to the redissolution of the membranes whilst drying. During precipitation, the osmotic pressure of water can reach up to 100 bar during precipitation. This is why water pushes the polymer solution aside when penetrating the protomembrane. With ongoing precipitation, the polymer-enriched phase solidifies, resulting in thin walls building the void filled supporting structure of the membrane [14,15,19].

3.3. Replacement of DMAc

After replacing THF, the next step was the replacement of DMAc with a more sustainable alternative. Even though CPME could not dissolve PSU when replacing THF, it was considered for a DMAc replacement because DMAc has a lower content of 15 wt% in the solvent system than THF at 60 wt%. Moreover, the aim of this study is to find a more sustainable solvent system, and CPME clearly is a more sustainable solvent than DMAc.

Firstly, THF was replaced again with NBP. In two separate approaches, DMAc was replaced once with 2M-THF (M4) and once with CPME (M5). THF was then replaced with 2M-THF and additionally DMAc was replaced with NBP (M6) and then with CPME (M7), separately.

No analyzable membranes could be produced in either solvent system with 2M-THF as a THF replacement (M6 and M7). When DMAc was replaced with CPME, PSU did not dissolve even after an extended period, preventing membranes from being fabricated. When DMAc was replaced by NBP, a solution was obtained, but after precipitation and drying the membrane was riddled with macroscopic defects in a way that no evaluable samples were obtained.

The membranes in which THF was replaced by NBP required longer times for the polymer to dissolve—usually twice as long as other membranes. The time required for precipitation was again 20 min. As a result, analyzable membranes were obtained.

When coating membranes prepared from NBP and 2M-THF (M4) with PDMS, it was found that those membranes changed from white to transparent again. In addition, it was impossible to remove such membranes without defects from the surface on which they were manufactured. Longer precipitation times or thermal treatment before coating could not completely solve the problem. Even though PSU membranes could not be coated, membranes prepared from solvent system M4 were measured in gas permeation...
experiments. Using NBP and CPME as the solvent system M5, no problems with PDMS coating were observed.

Cross-sections of membranes where both harmful solvents were replaced showed partially sponge-like membrane structures (Figure 5). The bottom layer of membranes made from NBP and CPME (solvent system M5) is in the macroscopic scale. The total thickness of this layer was 20 µm. A possible explanation for this layer is that phase separation or demixing occurred in the protomembrane before it was subjected to precipitation, leading to two layers. One layer filled with voids and one layer was without a structure. In the case of NBP and 2M-THF as the solvent system (M4), no macroscopic separation layer was observed and voids occurred beneath the top layer. In contrast to membranes where just THF was replaced, voids did not occur over the whole cross-section of those membranes (see Figure 4). Additionally, the voids were not drop-shaped but more finger-like structures. Beneath the void-filled part of those membranes, a sponge-like structure occurred with solvent system M4. Solvent system M5 showed a bottom layer without structure. This change in morphology is caused by different interactions between the changed solvents and polysulfone as well as changed miscibility of the solvents NBP and CPME/2M-THF compared to THF and DMAc. The first point addresses poor and good solvents. Poor solvents lead to a fast solvent exchange resulting in large voids, whereas good solvents show a delayed demixing with the polymer leading to sponge-like structures. The miscibility of the solvent and precipitation medium also affects the resulting membrane structure. If a low miscibility is given, a slow solvent exchange occurs resulting in a sponge-like morphology. If a high miscibility of solvent and precipitation medium is given, a fast solvent exchange occurs resulting in a finger-like or drop-shaped morphology [20]. Especially in membranes made from NBP and CPME (M5), a layer without structure was seen in the cross-section.

![Figure 5](image_url)

**Figure 5.** (a) Cross-section of a PSU membrane prepared from NBP and CPME. (b) Cross-section of a PSU membrane prepared from NBP and 2M-THF. The dashed lines indicate the bottom and top end of the membranes’ cross-section.

3.4. Variation of Precipitation Bath Temperature

All membrane structures obtained by more sustainable solvents revealed cross-sections with void-filled structures that are not as pressure resistant as sponge-like structures [60]. Since void formation is mainly caused by faster diffusion rates of water compared to organic solvents during precipitation, an easy way for suppressing void formation is to vary the precipitation bath temperature. Higher temperatures can facilitate the diffusion of organic solvents from the protomembrane into the precipitation medium, suppressing void formation. Cooling the precipitation bath can cause slower exchange and therefore slower penetration of water from the precipitation bath into the protomembrane. Both approaches are examined in this study.

Since membranes where both solvents were replaced by more sustainable alternatives revealed a defective separation layer, for this test series membranes with just a THF replacement were tested. The choice was 2M-THF because fabrication and gas separation
performance were closest to those of the standard recipe membranes. Additionally, the voids formed in membranes with 2M-THF as the THF alternative (M2) were larger and drop-like-shaped, resulting in less mechanically resistant membranes compared to membranes with NBP as the THF alternative (M1). Therefore, changes in the membrane structure are more significant in membranes made from 2M-THF compared to those made from NBP.

Lower Temperature of the Precipitation Bath

The first approach was to lower the temperature of the precipitation bath. The temperature was set to just over 0 °C, so that water in the precipitation bath remained liquid. In this case, water penetration from the precipitation bath into the protomembrane should be lowered in a way that the formation of voids is suppressed.

After producing PSU membranes at precipitation bath temperatures of 0 °C, membranes with an apparently smoother surface, less unevenness and fewer macroscopic defects were fabricated. The precipitation time had to be increased to 15 min due to insufficient precipitation after 4 min. Insufficient precipitation means that the amount of solvent in membranes after 4 min of precipitation was too high. As a result, membranes redissolved when left to dry. This can be explained by the slower solvent exchange at lower precipitation bath temperatures due to the lower diffusion of both water and organic solvents. Fifteen min was empirically found to be the shortest time for sufficient precipitation.

The structure shown in Figure 6 is a clear indicator for slower solvent exchange during precipitation. As mentioned before, lower temperatures of the precipitation bath cause decreased diffusion rates of water molecules into the protomembrane during precipitation. Therefore, the non-solidified polymer becomes a gel before it is pushed aside from penetrating water, resulting in a more sponge-like structure beneath a thicker separation layer. Additionally, this sponge-like structure leads to a decreased thickness of the membranes. The thickness is reduced by a factor of 2–3 compared to membranes precipitated at higher temperatures.

![Figure 6](image_url)

**Figure 6.** Cross-section of a PSU membrane prepared from 2M-THF as the THF alternative precipitated at 0 °C. The dashed lines indicate the bottom and top end of the cross-section.

Precipitation at 0 °C was shown to be an easy way of controlling the morphology of membranes where THF is replaced by 2M-THF. Additionally, membrane performance regarding permeances and permselectivities was not changed significantly as shown in Section 3.6. It was also noticed that permselectivities varied within the uncertainty of measurement compared to membranes precipitated at room temperature. The morphology of membranes precipitated at 60 °C is depicted in Figure 7.
Precipitation at 0 °C was shown to be an easy way of controlling the morphology of membranes where THF is replaced by 2M-THF. Additionally, membrane performance regarding permeances and permselectivities was not changed significantly as shown in Section 3.6. It was also noticed that permselectivities varied within the uncertainty of measurement compared to membranes precipitated at room temperature. The morphology of membranes precipitated at 60 °C is depicted in Figure 7.

Figure 7 shows that higher precipitation bath temperatures facilitate the diffusion of water molecules more strongly than the diffusion of organic solvent molecules during precipitation. This is in line with the findings of other research groups. The effect of the increased speed of water penetrating the protomembrane is seen by larger voids in membranes precipitated at 60 °C compared to membranes precipitated at room temperature or 0 °C. Because of the increased temperature, water penetrates the protomembrane faster during precipitation. As a result, the non-solidified polymer gel is pushed aside by penetrating water, forming walls between the voids. These larger voids lead to less mechanically stable membranes [60]. However, in the case of a defect-free separation layer, this structure would also lead to higher permeances compared to membranes prepared at lower precipitation bath temperatures. This is because gas transport away from the separation layer is much less hindered in membranes with large voids below the separation layer compared to membranes with a sponge-like support structure. In sponge-like support structures, there are more “walls”. This increases the resistance for gases to pass through. In a support structure filled with voids, there are fewer “walls” and therefore less resistance to gases.

3.5. Gas Permeation Measurements

To characterize the gas separation properties of all fabricated membranes, single-gas permeation measurements were conducted. The exact permeability of a membrane material is difficult to determine since the thickness of the selective layer varies over the whole membrane area. On the other hand, the thickness varies from membrane to membrane. As we showed in our previous paper, permeability is strongly dependent on the chain arrangement of the polymer inside the separation layer [18]. In this paper, the permeation behavior of the membranes is expressed as permeance, which is independent of the thickness of the gas separating layer or membrane in general.

To obtain a starting point for comparing membrane performance, a standard membrane made from THF, DMAc and MeOH (see Table 1) as well as a neat PDMS membrane were prepared and studied. The resulting permeances and permselectivities are shown in Tables 4 and 5.
Table 4. Permeances from the standard PSU membrane made from the solvent system THF, DMAc and MeOH, a PSU membrane from the literature with similar morphology and a neat PDMS membrane. Feed pressures: 390 mmHg (520 mbar) and 600 mmHg (800 mbar). Feed temperature: 30 °C.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>O₂</th>
<th>N₂</th>
<th>CO₂</th>
<th>CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard PSU</td>
<td>6.38×10⁻²</td>
<td>9.11×10⁻³</td>
<td>3.62×10⁻¹</td>
<td>1.28×10⁻²</td>
</tr>
<tr>
<td>Neat PSU [63] a</td>
<td>19.81</td>
<td>6.10</td>
<td>51.50</td>
<td>5.86</td>
</tr>
<tr>
<td>PDMS-coated PSU [63] a</td>
<td>6.30</td>
<td>1.15</td>
<td>8.91</td>
<td>0.61</td>
</tr>
<tr>
<td>Neat PDMS</td>
<td>6.34</td>
<td>2.98</td>
<td>30.66</td>
<td>9.55</td>
</tr>
</tbody>
</table>

*a measured at 29 °C and 750 mmHg (1000 mbar) via the variable volume method.

Table 5. Permselectivities for the standard PSU membrane made from the solvent system THF, DMAc and MeOH, a PSU membrane from the literature with similar morphology and a neat PDMS membrane. Feed pressures: 390 mmHg (520 mbar) and 600 mmHg (800 mbar). Feed temperature: 30 °C.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>O₂/N₂</th>
<th>CO₂/N₂</th>
<th>CO₂/CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard PSU</td>
<td>7.0</td>
<td>39.8</td>
<td>32.5</td>
</tr>
<tr>
<td>Neat PSU [63] a</td>
<td>3.49</td>
<td>8.44</td>
<td>8.14</td>
</tr>
<tr>
<td>PDMS-coated PSU [63] a</td>
<td>5.44</td>
<td>7.75</td>
<td>15.98</td>
</tr>
<tr>
<td>Neat PDMS</td>
<td>2.1</td>
<td>10.3</td>
<td>3.2</td>
</tr>
</tbody>
</table>

*a measured at 29 °C and 750 mmHg (1000 mbar) via the variable volume method.

The standard membrane made from harmful solvents showed on average an overall thickness of 94.1 μm. The permeances were low compared to values from the literature but permselectivities were significantly higher. An almost defect-free gas separation layer of the standard membrane can be assumed because permeances were clearly lower and permselectivities significantly higher than values from the literature.

The results of membranes made from more sustainable solvents and different precipitation temperatures are listed in Tables 6 and 7.

Table 6. Permeances of membranes made from more sustainable solvents. Temperatures in brackets give the temperature of the precipitation bath. If no temperatures are shown, room temperature is the temperature of the precipitation bath.

<table>
<thead>
<tr>
<th>Solvent System</th>
<th>O₂</th>
<th>N₂</th>
<th>CO₂</th>
<th>CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>4.84×10⁻²</td>
<td>8.78×10⁻³</td>
<td>2.78×10⁻¹</td>
<td>1.09×10⁻²</td>
</tr>
<tr>
<td>M2</td>
<td>5.91×10⁻²</td>
<td>8.84×10⁻³</td>
<td>4.00×10⁻¹</td>
<td>1.00×10⁻²</td>
</tr>
<tr>
<td>M4</td>
<td>225</td>
<td>289</td>
<td>235</td>
<td>364</td>
</tr>
<tr>
<td>M5</td>
<td>6.49×10⁻²</td>
<td>3.13×10⁻²</td>
<td>2.95×10⁻¹</td>
<td>4.82×10⁻²</td>
</tr>
<tr>
<td>M2 (0 °C)</td>
<td>6.02×10⁻²</td>
<td>9.47×10⁻³</td>
<td>3.75×10⁻¹</td>
<td>1.06×10⁻²</td>
</tr>
<tr>
<td>M2 (60 °C)</td>
<td>4.58×10⁻¹</td>
<td>2.38×10⁻¹</td>
<td>2.49</td>
<td>7.80×10⁻¹</td>
</tr>
</tbody>
</table>
Table 7. Permselectivity of membranes made from more sustainable solvents. Temperatures in brackets give the temperature of the precipitation bath. If no temperatures are shown, room temperature is the temperature of the precipitation bath.

<table>
<thead>
<tr>
<th>Solvent System</th>
<th>Overall Thickness [µm]</th>
<th>O₂/N₂</th>
<th>CO₂/N₂</th>
<th>CO₂/CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>138.2</td>
<td>5.7</td>
<td>32.7</td>
<td>28.8</td>
</tr>
<tr>
<td>M2</td>
<td>56.3</td>
<td>6.7</td>
<td>38.3</td>
<td>34.0</td>
</tr>
<tr>
<td>M4</td>
<td>121.5</td>
<td>0.94</td>
<td>0.86</td>
<td>0.64</td>
</tr>
<tr>
<td>M5</td>
<td>92.3</td>
<td>2.1</td>
<td>9.5</td>
<td>6.1</td>
</tr>
<tr>
<td>M2 (0 °C)</td>
<td>50.4</td>
<td>6.4</td>
<td>39.8</td>
<td>35.7</td>
</tr>
<tr>
<td>M2 (60 °C)</td>
<td>90.5</td>
<td>2.2</td>
<td>10.5</td>
<td>3.2</td>
</tr>
</tbody>
</table>

3.5.1. Replacement of THF

In comparison, the permeances of membranes with solvent systems M1 and M2 were quite similar to each other and to the permeances of the standard membrane (Table 4). These permeances lay in the same order of magnitude. On the other hand, oxygen and carbon dioxide permeances were higher in 2M-THF membranes compared to NBP membranes. Nitrogen showed the same permeance within the uncertainty of measurement. Methane showed a lower permeance in membranes prepared from 2M-THF. The difference in methane permeances in NBP and 2M-THF membranes should be treated with caution since the uncertainty of measurement for the gas permeation machine has almost been reached at such low values. The uncertainty of measurement for our setup lay at $2.22 \times 10^{-3}$ GPU. However, the changes of the permeances of oxygen and carbon dioxide are significant.

Obviously, permselectivities for all gas pairs were smaller in membranes prepared from solvent system M1 compared to solvent system M2. The decrease was 15–20% compared to standard and M2 membranes. These values indicate pinholes in NBP membranes. Those pinholes are closed by the PDMS coating. Since this coating showed lower permselectivities for all gas pairs, the resulting overall permselectivity is a mixture of permselectivities of the PSU membrane and the small areas where the PDMS coating is the only barrier between the feed and permeate room [56]. Therefore, the overall permselectivities in NBP membranes are lower. Merkel et al. showed permselectivities in PDMS for O₂/N₂, CO₂/N₂ and CO₂/CH₄ of 2.0, 7.0 and 3.2 at 35 °C, respectively [64].

The fact that the permeances of NBP membranes were slightly lower than those of 2M-THF membranes indicates that the area of defects is very low but still affecting the separation performance.

3.5.2. Replacement of THF and DMAc

Obviously, the non-coated membranes M4 showed high permeances and low permselectivities. The permeances were 3 to 5 orders of magnitude higher compared to all other membranes in this study. Additionally, the permeances of all gases did not differ by orders of magnitude, which leads to a poor separation effect. This indicates laminar flow or Knudsen diffusion occurring through those membranes. This means a separation effect is occurring, but it is dependent on the molecular weight of penetrating species. For calculating the separation effect via Knudsen diffusion, the following Equation (6) is used:

$$S_{i,j} = \sqrt{\frac{M_i}{M_j}}$$

(6)

where M is the molar mass of the diffusing gases i and j. Using Equation (6), permselectivities by Knudsen diffusion for the gas pairs O₂/N₂, CO₂/N₂ and CO₂/CH₄ are 0.94, 0.80 and 0.60, respectively. Small variations between the calculated and obtained Knudsen permselectivities arise from non-uniformly sized pores within the membrane. Therefore, non-coated membranes made from NBP and 2M-THF as THF and DMAc re-
placements (M4) are not suitable for gas separation applications but might be interesting as ultrafiltration membranes.

Membranes prepared from NBP and CPME (M5) showed higher permeances only for \( \text{N}_2 \) and \( \text{CH}_4 \), resulting in a poor separation effect. Permeances of those membranes did not reach those of neat PDMS membranes. PDMS showed permeances two orders of magnitude higher than membranes prepared from solvent system M5. Nevertheless, the permselectivity was equal to the separation performance of neat PDMS. This means membranes prepared from solvent system M5 contained defects meaning they were not able to separate gases. The flux remains low, since the number of defects is low in those membranes, resulting in a low gas flux and gas separation performance of PDMS membranes. These findings indicate that the combination of NBP and CPME is not suitable for gas separation membranes.

3.5.3. Replacement of THF and Varying Precipitation Temperatures

Permeances and separation performances remained at values of the solvent system M2 when M2 protomembranes were precipitated at 0 °C. The difference in permeances was in the range of 1.85–9.47%, where the largest changes were with nitrogen (+6.57%) and carbon dioxide (+9.47%). The smallest change in permeance was with oxygen (+1.85%). The differences in permeances reveal that these changes are likely due to the membrane. This means precipitation at lower temperatures may lead to changes on a molecular level of the membranes, resulting in changes in the fractional free volume. These changes in fractional free volume influence the diffusion of molecules and therefore permeance in polymeric membranes [56]. As all permeances increased, it is suggested that the polymer chains had less time to organize during precipitation due to the lower temperatures. This results in a higher fractional free volume compared to membranes precipitated at higher temperatures. This leads to higher permeances.

However, the permselectivities of gas pairs \( \text{CO}_2/\text{N}_2 \) and \( \text{CO}_2/\text{CH}_4 \) showed an opposite trend. The permselectivities were slightly increased compared to membranes precipitated at room temperature. These small changes can occur when permeances vary from measurement to measurement. The changes lay in the range of the type c uncertainty of measurement of our setup. This is also the explanation for why those permselectivities increased but the permselectivity of the gas pair \( \text{O}_2/\text{N}_2 \) slightly decreased.

In the second approach, a higher temperature was chosen for the precipitation bath. This should have an effect of organic solvents diffusing out of the protomembrane into the precipitation bath whilst precipitation. The temperature was set to 60 °C to facilitate the diffusion of organic solvents.

At this bath temperature, macroscopic defects were observed on the membrane surface, which increased in both number and size compared to membranes prepared at room temperature. Sampling therefore was more difficult. Nevertheless, it was possible to take samples without defects and to measure them successfully. The permeances of membranes precipitated at 60 °C were 1–2 orders of magnitude above those of membranes precipitated at room temperature. This indicates that the separation layer is defective or porous. However, PDMS showed permeances even one order of magnitude higher than those of membranes precipitated at 60 °C. This indicates that not just defects occurred in PSU membranes but that the membranes were in fact porous. The permselectivities reveal that only the PDMS protective layer had a separation effect. In this case, PSU membranes were not effectively separating gases but being a support for PDMS reducing the gas flux compared to neat PDMS.
3.6. Comparison with Literature

To evaluate the data acquired in this study, they were compared with those from the literature. An overview is given in Table 8.

Table 8. Separation performance of polysulfone membranes in this study and from the literature.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>(\text{O}_2/\text{N}_2)</th>
<th>(\text{CO}_2/\text{N}_2)</th>
<th>(\text{CO}_2/\text{CH}_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>5.7</td>
<td>32.7</td>
<td>28.8</td>
</tr>
<tr>
<td>M2</td>
<td>6.7</td>
<td>38.3</td>
<td>34.0</td>
</tr>
<tr>
<td>M4</td>
<td>0.94</td>
<td>0.86</td>
<td>0.64</td>
</tr>
<tr>
<td>M5</td>
<td>2.1</td>
<td>9.5</td>
<td>6.1</td>
</tr>
<tr>
<td>M2 (0 °C)</td>
<td>6.4</td>
<td>39.8</td>
<td>35.7</td>
</tr>
<tr>
<td>PSF [65]</td>
<td></td>
<td></td>
<td>36.4</td>
</tr>
<tr>
<td>PSF-DMF [66]</td>
<td>5.5</td>
<td>13.5</td>
<td>38.3</td>
</tr>
<tr>
<td>PSF-THF [66]</td>
<td>5.6</td>
<td>10.5</td>
<td>29.7</td>
</tr>
<tr>
<td>PSF-DMAc [66]</td>
<td>6.1</td>
<td>10.4</td>
<td>29.1</td>
</tr>
<tr>
<td>PSU [67]</td>
<td></td>
<td></td>
<td>23.12</td>
</tr>
<tr>
<td>PSF [68]</td>
<td></td>
<td></td>
<td>31.65</td>
</tr>
<tr>
<td>PSF [69]</td>
<td></td>
<td></td>
<td>22.0</td>
</tr>
<tr>
<td>PDMS [64]</td>
<td>2.0</td>
<td>7.0</td>
<td>3.2</td>
</tr>
</tbody>
</table>

\(^a\) precipitated at 0 °C. \(^b\) measured at 10 bar & 35 °C. \(^c\) measured at 5 bar. \(^d\) measured at 8 bar & 25 °C. \(^e\) measured at 35 °C.

It is obvious that precipitation temperature does not affect the separation performance of PSU membranes prepared with 2M-THF as the THF alternative (M2). This is a good indicator for reproducibility and a low value of defects in the gas separation layer. Moreover, membranes in this study showed a high separation performance for the gas pair \(\text{CO}_2/\text{N}_2\) compared to membranes from Maghami et al. [66].

It should be noted that no standardized measuring conditions exist in research for permeances or permeabilities. As such, the comparison of data from different sources is difficult. This is also why unitless permselectivities are shown in Table 8. Even this table should not be taken at face value because applied pressure and temperature during measurement have a large influence on the separation performance of membranes in general. As a rule of thumb, lower pressures and temperatures lead to higher separation performances but to lower permeances.

4. Conclusions

In this study, the existing membrane–solvent system PSU/THF/DMAc was attempted to be improved upon in terms of its sustainability without deteriorating the gas separation properties of PSU membranes. The morphology of those membranes should then be adjusted by varying selected process parameters to obtain a membrane without large voids. The membranes produced were assessed for their gas separation performance using the time-lag method. Visual representation was undertaken by SEM imaging.

The results of this study show that only THF can be replaced to maintain gas separation properties. Additionally, just two of three selected solvents, namely 2M-THF and NBP, were able to successfully replace THF without changing the recipe. It must be mentioned that, with NBP as THF alternative, precipitation times had to be chosen, changing from 4 min to at least 20 min to complete solvent exchange. Whenever THF was replaced, the sponge-like structure of PSU membranes changed to a void-filled membrane morphology when precipitated at room temperature. Replacing DMAc additionally to THF in all tests led to void-filled, porous membranes not capable of separating gases effectively.

For the first time in this study, we showed that by simply varying the temperature of the precipitation bath void formation could be suppressed in membranes prepared from solvent system M2 (2M-THF as the THF alternative). This means that even with the more sustainable solvent 2M-THF, a sponge-like membrane morphology can be obtained.
Summarizing all the data, a more sustainable solvent system was found to produce PSU gas separation membranes with a thin gas separation layer and a sponge-like support structure by using 2M-THF as the THF alternative and a temperature of the precipitation bath of 0 °C. Additionally, no decrease in permeance and gas separation performance was observed when 2M-THF was used for the casting solution and the precipitation bath temperature was set to 0 °C. Nevertheless, the precipitation time at 0 °C had to be adjusted to at least 15 min.

Future studies should deal with replacing DMAc and methanol with more sustainable solvents to eliminate all toxic and harmful solvents. Keeping permeances and gas separation performances on par with PSU flat sheet membranes prepared using traditional solvents is a further step. This approach would lead to PSU membranes for gas separation made from sustainable solvents, which is, in times of climate change and stricter regulations, more attractive for membrane producers and applicants.

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